

## NO DRAWINGS

(21) Application No. 55930/69 (22) Filed 14 Nov. 1969

(23) Complete Specification filed 5 Jan. 1971

(44) Complete Specification published 12 Sept. 1973

(51) International Classification C01B 31/02

(52) Index at acceptance C1A K4



## (54) METHOD OF MANUFACTURING CARBONACEOUS ARTEFACTS

(71) We, COAL INDUSTRY (PATENTS) LIMITED a Company organised in accordance with the Laws of Great Britain of Hobart House, Grosvenor Place, London, S.W.1, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns a method of manufacturing carbonaceous artefacts, comprising essentially glassy carbon.

The invention provides a method of producing an artefact consisting essentially of carbon wherein a thermoplastic alkaline phenol-aldehyde resin precursor mixture is heated at between 250°C and the carbonisation temperature of the mixture to form a thermoplastic product, the thermoplastic product is finely divided and the finely divided particles are shaped into a mass which is sintered and then carbonised to form the artefact.

The carbon product is in the form known as "glassy carbon" which is a hard, brittle, inert, isotropic carbon, lustrous on its fracture surfaces.

The aldehyde may be of any kind that reacts with phenols in alkaline conditions to form a resin. Desirably the aldehyde is an aldehyde having up to three carbon atoms. The preferred aldehyde is formaldehyde. Other suitable aldehydes includes furfural. The phenol may be of any kind that reacts with the aldehyde to form a resin under the alkaline conditions employed. Desirably the phenol has one phenolic hydroxyl group only, for example phenol, xylenol, cresol and naphthol. Other suitable phenols include resorcinol. Mixtures of one or more phenols or of one or more aldehydes, or both, may be employed.

The thermoplastic alkaline phenol-aldehyde resin precursor mixture need not contain an aldehyde itself. If it does not contain an aldehyde it should contain a substance releas-

ing, or reacting with the phenol so as to release an aldehyde on heating, for example hexamine. A preferred mixture is formed by the admixture of phenol and hexamine.

Advantageously, an excess of phenol is employed. Preferably an amount of phenol just sufficient to react with the aldehyde without substantial cross-linking is employed.

The alkaline phenol-aldehyde thermoplastic resin precursor mixture is then heated to a temperature of between about 250°C and the carbonisation temperature of the mixture. This temperature is that at which the mixture blackens or darkens, because of cross-linking. As a general guide a temperature of up to 350°C is suitable and a preferred range is between 300°C. and 350°C. An atmosphere substantially inert to the resin is desirably employed. The function of this initial heating is not fully understood. Excess phenol and, if appropriate, ammonia, are liberated. In particular, the temperature is much higher than those normally envisaged for phenolic resins. It is resumed that the treatment produces long polymer chains which coalesce on sintering.

The thermoplastic product is then cooled and the solid thermoplastic product crushed to a fine powder. The powder may then be compacted at a relatively high pressure before sintering. If a non-porous carbon artefact is required, it will normally be essential to compact the finely divided resinous product, for example in a die. The compaction may be at an elevated temperature if desired. The porosity of the products may be varied by varying the conditions of compaction, including the particle size and the compacting loads.

The sintering is preferably carried out in an inert atmosphere. A relatively low pressure, for example between 1 and 20 lb/in<sup>2</sup>, may be employed during sintering.

The sintering is preferably carried out with a gradually increasing temperature for such time that the required degree of porosity is achieved. For example, a heating rate of 1°C/min to 3°C/min up to 250°C to 340°

C may be employed. The artefact may then be carbonised in a conventional manner, for example by heating in an inert atmosphere to between 900°C and 1200°C, thereby being converted to glassy carbon.

The invention includes also artefacts made according to the above method.

The method of the present invention enables artefacts consisting essentially of glassy carbon to be manufactured more rapidly and the porosity adjusted more easily than hitherto proposed methods.

The following example illustrates the method according to the invention.

Bulk phenol-hexamine mixture in a molar ratio of 12:1 is heated to a temperature of 330°C in a nitrogen atmosphere for a period of 15 mins. The heated material is then ground in a ball mill to -350 B.S.S. mesh to produce finely divided phenol-hexamine thermoplastic material.

The thermoplastic material is placed in a steel die and compacted at the relatively high pressure of 20 tons/in<sup>2</sup> at ambient temperature to produce a disc-shaped compact which is subsequently removed from the die.

The compact is sintered by heating at a rate of 2°C/min to a temperature of 330°C in a nitrogen atmosphere for 15 mins to produce a non-porous body. The relatively light pressure of 20 lb/in<sup>2</sup> is applied to the compact at the said temperature of 330°C.

The body is heated at a rate of 2°C/min up to 400°C and thence to a temperature of 1000°C in a nitrogen atmosphere to produce a glassy carbon artefact. The body is held at the temperature of 1000°C for about 10 minutes.

The resulting glassy carbon artefact has the following properties.

Density 1.5 g/cm<sup>3</sup>

Electrical Resistivity 0.001 ohm cm.

Weight loss in oxidising gas at 700°C. in dry air 5 g/m<sup>2</sup>/hr.

#### 45 WHAT WE CLAIM IS:—

1. A method of producing an artefact consisting essentially of carbon wherein a thermo-

plastic alkaline phenol-aldehyde resin precursor mixture is heated at between 250°C and the carbonisation temperature of the mixture to form a thermoplastic product, the thermoplastic product is finely divided and the finely divided particles are shaped into a mass which is sintered and then carbonised to form the artefact.

2. A method as claimed in claim 1 wherein the aldehyde of the thermoplastic alkaline phenol-aldehyde resin precursor mixture has up to 3 carbon atoms.

3. A method as claimed in claim 2 wherein the aldehyde is formaldehyde.

4. A method as claimed in any of the preceding claims wherein the phenol of the thermoplastic alkaline phenol-aldehyde resin precursor mixture has one phenolic hydroxyl group only.

5. A method as claimed in claim 4 wherein the phenol is phenol.

6. A method as claimed any of the preceding claims wherein the thermoplastic alkaline phenol-aldehyde resin precursor mixture contains hexamine.

7. A method as claimed in any of the preceding claims wherein the thermoplastic alkaline phenol-aldehyde resin precursor mixture is heated at between 300°C and 350°C.

8. A method as claimed in any of the preceding claims wherein the shaping is carried out by compaction.

9. A method as claimed in claim 8 wherein the compaction is carried out at an elevated temperature.

10. A method as claimed in any of the preceding claims wherein the thermoplastic product is sintered at a temperature of up to 250°C to 340°C.

11. A method substantially as described herein with reference to the example.

12. Artefacts consisting essentially of carbon whenever manufactured by a process as claimed in any of the preceding claims.

For the Applicants,

J. I. WOOD,

Chartered Patent Agent.